

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
14 October 2004 (14.10.2004)

PCT

(10) International Publication Number  
**WO 2004/088673 A1**

(51) International Patent Classification<sup>7</sup>: **H01B 1/12**,  
B01D 71/68

(21) International Application Number:  
PCT/GB2004/001375

(22) International Filing Date: 1 April 2004 (01.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0307606.4 2 April 2003 (02.04.2003) GB

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ION-CONDUCTING POLYMERIC MATERIALS

(57) Abstract: A method of preparing a relatively stable solution and/or dispersion of an ion-conducting polymeric material, for example one comprising phenyl moieties, carbonyl and/or sulphone moieties and ether and/or thioether moieties, comprises: (a) selecting a solvent mixture comprising water and a first organic solvent in which mixture said ion-conducting polymeric material can be dissolved and/or dispersed; (b) dissolving and/or dispersing said ion-conducting polymeric material in said solvent mixture; and (c) removing greater than 80% of the total amount of said first organic solvent in said solvent mixture, thereby to leave a formulation comprising said ion-conducting polymeric material dissolved and/or dispersed in a solvent formulation comprising a major amount of water.



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## ION-CONDUCTING POLYMERIC MATERIALS

This invention relates to ion-conducting polymeric materials and particularly, although not exclusively, relates to a method of preparing a formulation of an ion-conducting polymeric material and such a formulation per se. Preferred embodiments relate to the use of formulations prepared in the manufacture of coatings or films of ion-conducting polymeric materials.

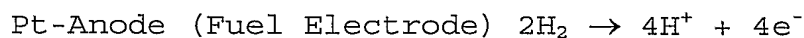
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One type of polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

15

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:

20



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:

25



30

Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an

external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

Preferred ion-conducting polymeric materials for use as components of polymer electrolyte membranes in fuel cells have high conductivity (low EW, or high ion-exchange capacities), optimum water uptake for good conductivity and mechanical properties and solubility in solvents which can be used to cast the membranes.

10

Examples of known ion-conducting polymeric materials are described in US 5985477 (Sumitomo) and US 5906716 (Hoechst). The polyaryletherketones and/or sulphones described are dissolved in a solvent, usually N-methylpyrrolidone (NMP), and are then cast to prepare membranes.

Whilst NMP is a very good solvent for casting membranes from a wide range of materials, membranes cast from NMP (especially polymer electrolyte membranes of fuel cells) can have defects and/or exhibit problems in downstream process steps. Furthermore, it is preferred for environmental and safety reasons to minimise the amounts of organic solvents used in chemical processes.

25

It is an object of the present invention to address problems associated with the preparation and/or use of formulations of ion-conducting polymeric materials.

According to a first aspect of the present invention, there is provided a method of preparing a formulation comprising an ion-conducting polymeric material, the method comprising:

- (a) selecting an ion-conducting polymeric material of a type which includes:
- (i) phenyl moieties;
  - 5 (ii) carbonyl and/or sulphone moieties; and
  - (iii) ether and/or thioether moieties;
- (b) selecting a solvent mixture comprising water and a first organic solvent in which mixture said ion-
- 10 conducting polymeric material can be dissolved and/or dispersed;
- (c) dissolving and/or dispersing said ion-conducting polymeric material in said solvent mixture;
- 15 (d) removing greater than 80% of the total amount of said first organic solvent in said solvent mixture, thereby to leave a formulation comprising said ion-conducting polymeric material dissolved and/or
- 20 dispersed in a solvent formulation comprising a major amount of water.

Surprisingly, it has been found that a stable solution and/or dispersion of the polymeric material in a

25 substantial amount of water can be prepared in the method which solution/dispersion would not generally be preparable by simply attempting to dissolve/disperse the polymeric material in a solvent formulation comprising the same amount of water, without the use of steps (b) to (d)

30 of the method.

The formulations prepared in the method appear to the naked eye to be solutions; however, they are probably not

true solutions but more likely are very fine dispersions of the ion-conducting polymeric material in the solvent formulation.

5 Said first organic solvent selected in step (b) is preferably water miscible at 25°C. Said first organic solvent preferably has a boiling point of less than that of water. The boiling point of the first organic solvent may be less than 95°C, suitably less than 90°C, preferably  
10 less than 85°C, more preferably less than 80°C, especially less than 75°C, at atmospheric pressure. The boiling point may be greater than 30°C, suitably greater than 40°C, preferably greater than 50°C, more preferably greater than 55°C at atmospheric pressure.

15

Said first organic solvent may have up to five, preferably up to four, carbon atoms. Preferably, said first organic solvent has two to four carbon atoms. Said first organic solvent preferably includes an hydroxy, ether or carbonyl  
20 functional group. Preferably, said first organic solvent includes only one of said functional groups. Said first organic solvent preferably does not include any other functional groups. Said first organic solvent preferably does not include any halogen atoms. Said first organic  
25 solvent is preferably saturated. Said solvent may be selected from alcohols, ethers (including cyclic ethers) and ketones, especially C<sub>2-4</sub> alcohols, ethers and ketones. Especially preferred first organic solvents are acetone, methylethylketone, ethanol and tetrahydrofuran.

30

Said solvent mixture selected in step (b) may include more than one organic solvent and each may be as described in any statement herein.

In one embodiment, said solvent mixture may include an optional second organic solvent. Said second organic solvent may have a boiling point which is greater than that of said first organic solvent so that said first organic solvent is preferentially removed in step (d) and, preferably, less than 10 wt%, more preferably less than 5 wt%, especially less than 1 wt%, of said second organic solvent is removed in step (d). Said second organic solvent may have a boiling point at atmospheric pressure which is at least 20°C greater than the boiling point of said first organic solvent. Said second organic solvent may be included to facilitate the preparation of articles, for example films, in accordance with the third aspect described hereinafter. Said second organic solvent may act as a coalescing agent during film formation. However, it is preferred for said second organic solvent to be included (if included at all) after step (d). Examples of second solvents are N-methylpyrrolidene and glycols such as ethylene glycol.

The ratio of the wt% of water to the wt% of said first organic solvent (preferably to the wt% of the total amount of organic solvent(s) in the mixture) is suitably in the range 0.25 to 2.5, preferably in the range 0.4 to 2.3 and, more preferably, in the range 0.5 to 1.5.

Suitably, said solvent mixture of step (c) includes at least 1 wt%, preferably at least 3 wt%, more preferably at least 7 wt%, especially at least 9 wt% of said ion-conducting polymeric material. Said solvent mixture may include less than 20 wt%, preferably less than 15 wt%,

especially less than 12 wt% of said ion-conducting polymeric material.

Step (c) of the method is preferably carried out at a temperature which is less than the boiling point of the solvent mixture. Thus, step (c) preferably comprises dissolving and/or dispersing said ion-conducting polymeric material in said solvent mixture under conditions at which said solvent mixture is not boiling. Suitably, step (c) is carried out at ambient temperature (eg 20°C) or above and at less than the boiling point of said solvent mixture.

Step (d) suitably includes removing greater than 85%, preferably greater than 90%, more preferably greater than 95 wt%, especially greater than 99 wt% of said first organic solvent in step (d). Preferably, substantially the entirety of said first organic solvent is removed in step (d).

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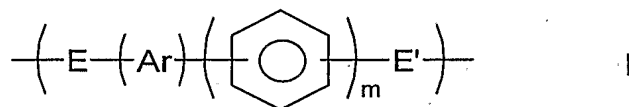
Said first organic solvent is preferably evaporated off in step (d), suitably under a pressure of less than atmospheric pressure. After removal of the first organic solvent, the solvent formulation which includes a major amount of water suitably includes at least 10 wt%, preferably at least 14 wt%, more preferably at least 18 wt% of said ion-conducting polymeric material in said solvent formulation. The solvent formulation may include less than 30 wt% or less than 25 wt% of said ion-conducting polymeric material. However, a solvent formulation which is more concentrated in said ion-conducting polymeric material may be prepared by removing, for example evaporating, some of the water in the solvent

formulation which includes a major amount of water. In this event, said solvent formulation which includes a major amount of water may include at least 30 wt%, at least 40 wt% or even 50 wt% of said ion-conducting  
 5 polymeric material.

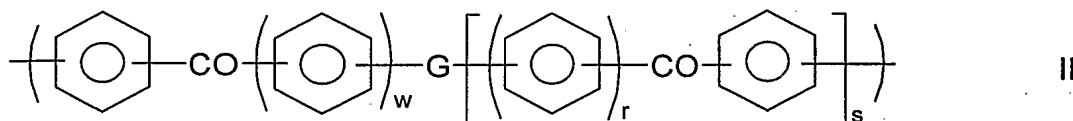
Said ion-conducting polymeric material may include

a moiety of formula

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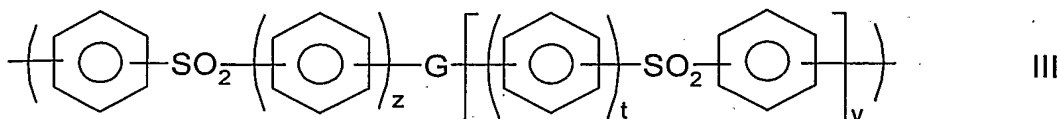


and/or a moiety of formula



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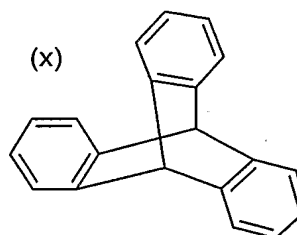
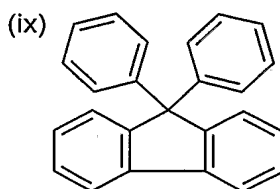
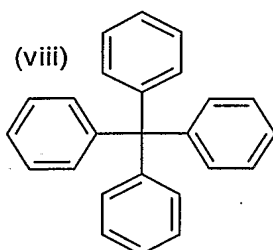
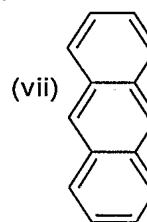
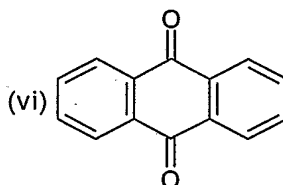
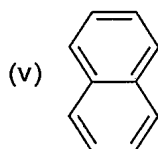
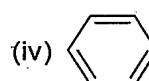
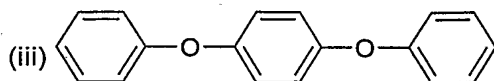
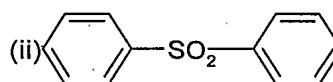
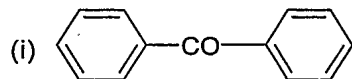
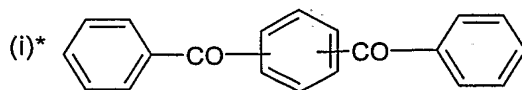
and/or a moiety of formula



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wherein at least some of the units I, II and/or III are functionalised to provide ion-exchange sites, wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and  
5 wherein m,r,s,t,v,w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from  
10 one of the following moieties (i)\* or (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties



Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to  
5 moieties to which it is bonded.

In (i)\*, the middle phenyl may be 1,4- or 1,3- substituted.

Suitably, to provide said ion exchange sites, said  
10 polymeric material is sulphonated, phosphorylated,  
carboxylated, quaternary-aminoalkylated or

chloromethylated, and optionally further modified to yield  
-CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>, -CH<sub>2</sub>NR<sub>3</sub><sup>20+</sup> where R<sup>20</sup> is an alkyl, or -CH<sub>2</sub>NAr<sub>3</sub><sup>x+</sup> where  
Ar<sup>x</sup> is an aromatic (arene), to provide a cation or anion  
exchange membrane. Further still, the aromatic moiety may  
5 contain a hydroxyl group which can be readily elaborated by  
existing methods to generate -OSO<sub>3</sub>H and -OPO<sub>3</sub>H<sub>2</sub> cationic  
exchange sites on the polymer. Ion exchange sites of the  
type stated may be provided as described in WO95/08581.

10 Preferably, said polymeric material is sulphonated.  
Preferably, the only ion-exchange sites of said polymeric  
material are sites which are sulphonated.

References to sulphonation include a reference to  
15 substitution with a group -SO<sub>3</sub>M wherein M stands for one or  
more elements selected with due consideration to ionic  
valencies from the following group: H, NR<sub>4</sub><sup>y+</sup>, in which R<sup>y</sup>  
stands for H, C<sub>1</sub>-C<sub>4</sub> alkyl, or an alkali or alkaline earth  
metal or a metal of sub-group 8, preferably H, NR<sub>4</sub><sup>+</sup>, Na, K,  
20 Ca, Mg, Fe, and Pt. Preferably M represents H.  
Sulphonation of the type stated may be provided as  
described in WO96/29360.

Said polymeric material may include more than one different  
25 type of repeat unit of formula I; more than one different  
type of repeat unit of formula II; and more than one  
different type of repeat unit of formula III.

Said moieties I, II and III are suitably repeat units. In  
30 the polymeric material, units I, II and/or III are suitably  
bonded to one another - that is, with no other atoms or  
groups being bonded between units I, II, and III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred  
5 alkyl groups are C<sub>1-10</sub>, especially C<sub>1-4</sub>, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional  
10 substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Another group of optional substituents of the phenyl  
15 moieties in units I, II or III include alkyls, halogens, C<sub>y</sub>F<sub>2y+1</sub> where y is an integer greater than zero, O-R<sup>q</sup> (where R<sup>q</sup> is selected from the group consisting of alkyls, perfluoralkyls and aryls), CF=CF<sub>2</sub>, CN, NO<sub>2</sub> and OH. Trifluormethylated phenyl moieties may be preferred in some  
20 circumstances.

Where said polymeric material is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its  
25 swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via  
30 sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene  
5 moieties have 1,4- linkages.

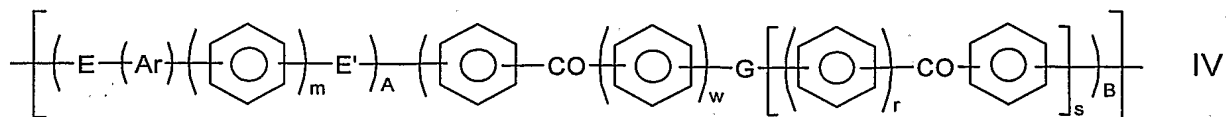
Preferably, the polymeric chain of the first material does not include a -S- moiety. Preferably, G represents a direct link.

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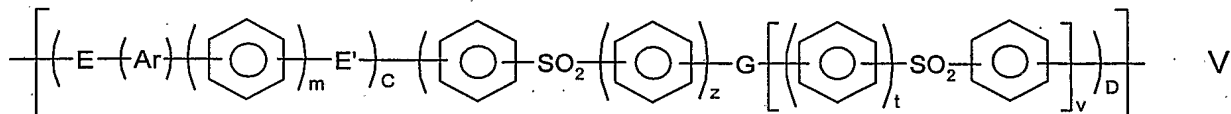
Suitably, "a" represents the mole % of units of formula I in said polymeric material, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said material, suitably wherein each unit II is the  
15 same; and "c" represents the mole % of units of formula III in said material, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55,  
20 more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about  
25 100. Preferably, said polymeric material consists essentially of moieties I, II and/or III.

Said polymeric material may be a homopolymer having a repeat unit of general formula

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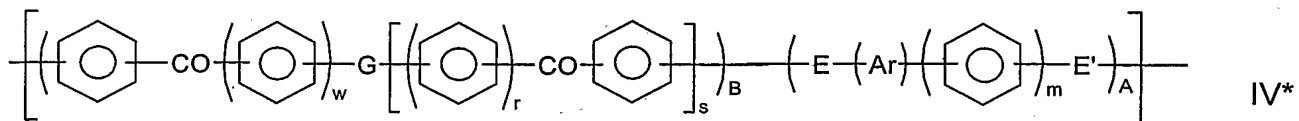
or a homopolymer having a repeat unit of general formula



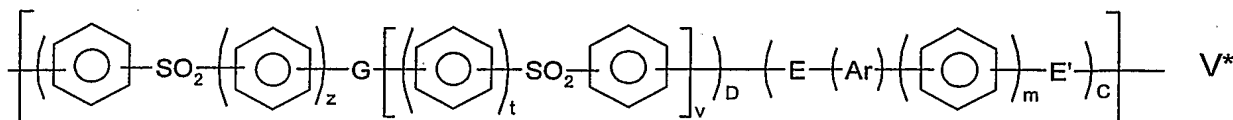
or a random or block copolymer of at least two different units of IV and/or V provided that repeat units (or parts of repeat unit) are functionalised to provide ion-exchange sites;

wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

As an alternative to a polymer comprising units IV and/or V discussed above, said polymeric material may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula

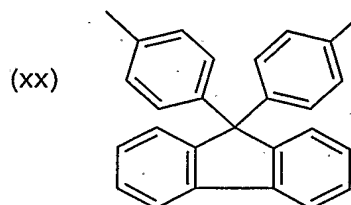
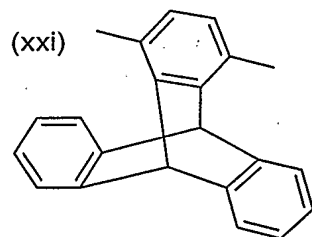
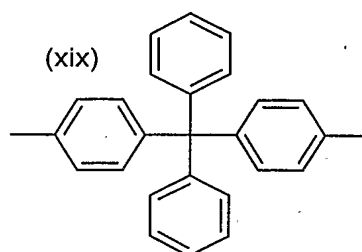
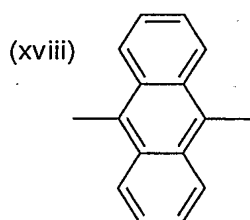
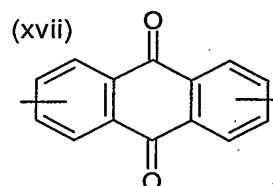
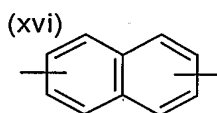
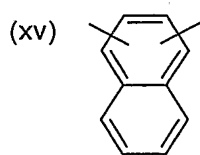
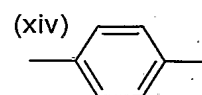
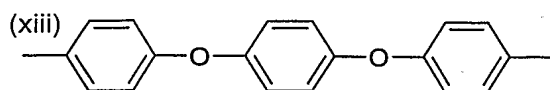
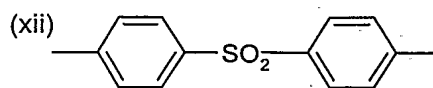
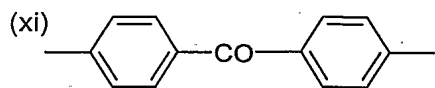
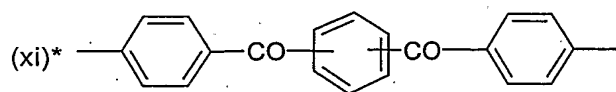


or a random or block copolymer of at least two different units of IV\* and/or V\* provided that repeat units (or parts of repeat units) are functionalised to provide ion-exchange

sites; wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

- 5 Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1.
- 10 Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties (xi)\* and (xi) to (xxi):



In (xi)\*, the middle phenyl may be 1,4- or 1,3-substituted.



Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5-moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7-moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

5

Unless otherwise stated in this specification, a reference to a crystalline material extends to any material having at least some crystallinity.

- 10 The existence and/or extent of crystallinity in a polymer is preferably measured by wide angle X-ray diffraction, for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Alternatively, Differential Scanning Calorimetry (DSC) could be used to assess crystallinity.
- 15 The level of crystallinity in said polymeric material may be 0% (e.g. where the material is amorphous or crystallisable); or the level of crystallinity may be at least 0.5%, suitably at least 1%, preferably at least 5% weight fraction, suitably when measured as described by
- 20 Blundell and Osborn. The level of crystallinity in said polymeric material may be less than 20%.

Suitable moieties Ar are moieties (i)\*, (i), (ii), (iv) and (v) and, of these, moieties (i)\*, (i), (ii) and (iv) are

25 preferred. Preferred moieties Ar are moieties (xi)\*, (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi)\*, (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative first

30 polymeric materials comprising units IV\* and/or V\*, preferred Ar moieties are (v) and, especially, (xvi).

One preferred class of polymeric materials may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO<sub>2</sub>- moieties between aryl (or other  
5 unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first aspect does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

10 Preferred polymeric materials include -ether-biphenyl-ether-phenyl-ketone- units. Preferred polymeric materials may additionally include -ether-phenyl-sulphone-phenyl-ether-phenyl-ketone- units. Optionally, preferred polymeric materials may include -ether-phenyl-sulphone-  
15 phenyl-ether-phenyl-ketone- units.

Where a phenyl group is sulphonated, it may be mono-sulphonated.

20 The glass transition temperature ( $T_g$ ) of said ion-conducting polymeric material may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the  $T_g$  may be at least 170°C, or at least 190°C  
25 or greater than 250°C or even 300°C.

Said polymeric material may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7  
30 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm<sup>-3</sup>, said solution containing 1g of polymer per 100cm<sup>-3</sup> of

solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm<sup>3</sup>, said solution containing 0.1g of polymer per 100cm<sup>3</sup> of solution. The measurements of both RV and IV both suitably employ a  
5 viscometer having a solvent flow time of approximately 2 minutes.

The equivalent weight (EW) of said ion-conductive polymeric material is preferably less than 850g/mol, more preferably  
10 less than 800g/mol, especially less than 750g/mol. The EW may be greater than 300, 400 or 500 g/mol.

The boiling water uptake of ion-conductive polymeric material measured as described hereinafter is suitably less  
15 than 350%, preferably less than 300%, more preferably less than 250%.

The main peak of the melting endotherm (T<sub>m</sub>) for said first polymeric material may be at least 300°C.

20

According to a second aspect of the invention, there is provided a polymeric material containing formulation (hereinafter "said pmc formulation") which comprises an ion-conducting polymeric material dissolved and/or  
25 dispersed in a solvent formulation wherein:

(a) said ion-conducting polymeric material includes:

- (i) phenyl moieties;
- (ii) carbonyl and/or sulphone moieties; and
- 30 (iii) ether and/or thioether moieties; and

(b) greater than 50 wt% of said solvent formulation is made up of water.

Suitably, at least 55 wt%, preferably at least 60 wt%, of said solvent formulation is made up of water. In embodiments wherein a second organic solvent is included in said solvent mixture, said pmc formulation may include a second organic solvent as described above. Said solvent formulation of said second aspect may include 0-40 wt% of said second solvent formulation. In preferred embodiments at least 95 wt%, especially at least 99 wt% of said solvent formulation of the second aspect is made up of water. In especially preferred embodiments, said solvent formulation consists essentially of water.

Said pmc formulation may include at least 1 wt%, suitably at least 3 wt%, preferably at least 7 wt%, more preferably at least 9 wt% of said ion-conducting polymeric material (or if more than one type of polymeric material is included, the total amount of polymeric materials may be as aforesaid). In some situations, said pmc formulation may include greater than 30 wt%, or even greater than 40 wt% of said polymeric material(s).

The pmc formulation is preferably a stable solution/dispersion - that is, the polymeric material does not substantially precipitate over time.

According to a third aspect of the present invention, there is provided a method of fabricating an article, the method including the step of contacting a member with a formulation according to the first or second aspects. The method may be used to deposit the polymeric material on said member. For example, said member may be a support which may be contacted with said formulation in order to

prepare a membrane; or said support may be coated with said formulation and/or said ion-conducting polymeric material in order to prepare an article which comprises said member and a coating prepared as described.

5

The method of the third aspect may be used in fabricating a wide range of types of articles. In one embodiment, said formulation may be used to impregnate a said member, for example a fibre or fabric. In this event, said solvent mixture may not include a said second organic solvent as described above. In another embodiment, said formulation may be used to form a film in which case, said solvent mixture may include a said second organic solvent. In either case, the method may be advantageous since said solvent mixture includes a major amount of water, rather than a major amount of organic solvent and is consequently easier to handle. Furthermore, it is found that a formulation according to the first or second aspects may include a relatively high concentration of said polymeric material (eg greater than 50 wt%) and, therefore, removal of solvents from the formulation after contact with said member may require less energy.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

Example 1a

A 700ml flanged flask fitted with a ground glass Quickfit  
5 lid, stirrer/stirrer guide, nitrogen inlet and outlet was  
charged with 4,4'-difluorobenzophenone ( 89.03g, 0.408  
mole, mole ratio = 1.02), 4,4'-dihydroxybiphenyl (24.83g,  
0.133 mole, mole ratio = 0.33), 4,4'-  
dihydroxydiphenylsulphone (53.65g, 0.213 mole, mole ratio  
10 = 0.536), 4,4'-dihydroxybenzophenone (11.37g, 0.053 mole,  
mole ratio = 0.134) and diphenylsulphone (332g) and purged  
with nitrogen for over 1 hour. The contents were then  
heated under a nitrogen blanket to between 140 and 150°C  
to form an almost colourless solution. While maintaining  
15 a nitrogen blanket, dried sodium carbonate (43.24g, 0.408  
mole) was added. The temperature was raised gradually to  
320°C over 3 hours then maintained for 1.5 hours.

The reaction mixture was allowed to cool, milled and  
20 washed with acetone and water. The resulting polymer was  
dried in an air oven at 120°C. The polymer had a melt  
viscosity at 400°C, 1000sec<sup>-1</sup> of 0.34 kNsm<sup>-2</sup>.

Example 2a

25

A 700ml flanged flask fitted with a ground glass Quickfit  
lid, stirrer/stirrer guide, nitrogen inlet and outlet was  
charged with 4,4'-difluorobenzophenone (89.03g, 0.408  
mole, mole ratio = 1.02), 4,4'-dihydroxybiphenyl, (24.93g,  
30 0.133 mole, mole ratio = 0.33), 4,4'-  
dihydroxydiphenylsulphone (66.73g, 0.267 mole, mole ratio  
= 0.67) and diphenylsulphone (332g) and purged with  
nitrogen for over 1 hour. The contents were then heated

under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution.. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.40 mole) and potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.28 kNsm<sup>-2</sup>.

By processes analogous to Examples 1a and 2a, further materials were prepared. A summary of the examples including mole ratios used in the preparations and Melt viscosities (MV) achieved are provided in Table A below, wherein the following abbreviations are used:

BDF 4,4'-difluorobenzophenone  
 BP 4,4'-dihydroxybiphenyl  
 DHB 4,4'-dihydroxybenzophenone  
 Bis-S 4,4'-dihydroxydiphenylsulphone

TABLE A

Polymer	Polymer Composition (mole ratio)				MV KNsm <sup>-2</sup>
	BDF	BP	DHB	Bis-S	
1a	1.02	0.33	0.134	0.536	0.34
1b	1.02	0.33	0.134	0.536	0.61
2a	1.02	0.33	-	0.67	0.28
2b	1.02	0.33	-	0.67	0.40

### Example 3 - Sulphonation of polymers

The polymers of Examples 1 and 2 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, titration confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit.

### Example 4 - Membrane fabrication using NMP

Membranes were produced from the polymers of Examples 1 and 2 after sulphonation as described in Example 3 by dissolution of the sulphonated polymers in NMP (N-methylpyrrolidone) to form homogenous solutions, casting the solutions onto clear glass plates followed by drawing down, using a Gardner knife, to give 400 micron films. The NMP was then evaporated.

### Example 5 - Boiling Water Uptake

The following general procedure was followed to determine the Boiling Water Uptake of the membranes prepared.

5cm x 5cm samples of membranes were selected. The thickness of the samples was related to the concentration of polymers in the solvent systems used to cast the



membranes. The membranes were separately immersed in boiling deionised water (500ml) for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptake was calculated as described below:

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Table B below provides results for the polymers of Examples 1 and 2 when fabricated as described in Example 4. EW refers to the "equivalent weight".

TABLE B

Sulphonated Polymer from	EW Theoretical	EW Actual	Boiling Water Uptake (%)
1a	683	677	143
1b	683	683	128
2a	690	694	140
2b	690	699	144

Example 6 - Membrane fabrication using water-based solvent formulations

Membranes were produced as described in Example 4, except that the sulphonated polymers were dissolved in a 50:50 mixture of acetone/water including 5 wt% NMP, at a sulphonated polymer concentration of 10 wt%. Dissolution may be undertaken at any temperature between ambient temperature and the boiling point of the solvent mixture. The falling ball viscosity of the above solutions was

measured at 23°C using a Gilmont (Trade Mark) Instruments Falling Ball Viscometer using a stainless steel ball. Results for each solution, together with values for the boiling water uptake, measured as described in Example 5, are provided in Table C below.

TABLE C

Sulphonated Polymer from	Falling Ball Viscosity (cP)	Boiling Water Uptake (%)
1a	892	106
1b	1227	102
2a	174	140
2b	417	147

10

Example 7 - Preparation of dispersions of sulphonated polymers in water and membrane fabrication

Example 7(a)

15

The sulphonated polymers were each dissolved in a 50:50 mixture of acetone and water and, subsequently, the acetone was removed using a rotary evaporator under reduced pressure (20mm Hg/40°C), leaving approximately 20 wt% sulphonated polymer in water. The formulation produced is probably not a true solution but is more likely a very fine dispersion of the sulphonated polymer in water. The dispersions had very low viscosities and membranes cast therefrom tended to be brittle. However, the formulations could be used to impregnate fibres or fabrics and this may be facilitated by their low viscosities. Table D details the viscosity "before evaporation" for the formulations.

25

Example 7(b)

The procedure of Example 7(a) was followed except that,  
5 after removal of the acetone, some of the water was  
removed by using a rotary evaporator (20mm Hg/70°C) to  
produce more concentrated solutions (up to 50 wt% of  
sulphonated polymer in water). The formulation could be  
used to produce membranes. Table D details the viscosity  
10 of the formulations "after evaporation" of water, together  
with the "final concentration" of sulphonated polymer.

TABLE D

Sulphonated polymer from	Falling ball viscosity (cP)		Final conc. Of sulphonated polymer (% w/w)
	Before evaporation	After evaporation	
1a	82	282	36
1b	23	314	49
2a	18	480	54
2b	21	680	53

15

Example 7(c)

The procedure of Example 7(b) was followed, except that a  
20 coalescing agent (NMP or ethylene glycol) was added as  
detailed in Table E to facilitate preparation of  
membranes. Membranes were prepared and boiling water  
uptakes (%) determined as described above. Results are  
provided in Table E below.

25

TABLE E

Sulphonated Polymer from	EW Theoretical	EW Actual	Amount NMP (wt%)	Final conc. of sulphonated polymer (%w/w)	Boiling Water Uptake (%)
1a	683	691	10	32	106
1b	683	701	15	42	102
2a	690	710	15	46	135
2b	690	709	15	45	158

5. It should be appreciated from Table E that no increase in EW is observed, suggesting the procedure described does not cause a loss of sulphonic acid groups.

10 Example 8 - Membrane fabrication using water-based solvent formulations

Membranes were produced as described in Example 4, except that the sulphonated polymers were dissolved in a 50:50 mixture of THF/water including 5 wt% NMP, at a sulphonated polymer concentration of 10 wt%. The values for the boiling water uptake measured as described in Example 5, are provided in Table F below. The falling ball viscosity of the above solutions were measured at 23°C using a Gilmont® Instruments Falling Ball Viscometer using a stainless steel ball.

TABLE F

Sulphonated Polymer from	Falling Ball Viscosity (cP)	Boiling Water Uptake (%)
1a	1034	109
2a	4964	136

Example 9 - Preparation of dispersions of sulphonated polymers in water and membrane fabrication

Example 9(a)

5

The sulphonated polymers were each dissolved in a 50:50 mixture of THF and water and, subsequently, the THF was removed using a rotary evaporator under reduced pressure (20mm Hg/40°C), leaving approximately 17 wt% sulphonated polymer in water. The formulation produced is probably not a true solution but is more likely a very fine dispersion of the sulphonated polymer in water. The dispersion had very low viscosity and membranes cast therefrom tended to be brittle. The aqueous solutions/dispersions could be used to impregnate fibres of fabrics. Table G details the viscosity "before evaporation" for the formulations.

Example 9 (b)

20

The procedure of Example 9(a) was followed except that, after removal of the THF, some of the water was removed by using a rotary evaporator (20mm Hg/70°C) to produce more concentrated solutions. The formulation could be used to produce membranes. Table G details the viscosity of the formulations "after evaporation" of water, together with the concentration of sulphonated polymer.

TABLE G

Sulphonated polymer from	Falling ball viscosity (cP)		Sulphonated polymer conc. (% w/w)
	Before evaporation	After evaporation	
1a	50	104	22
2a	800	1068	21

5 Example 9(c)

The procedure of Example 9(b) was followed, except that a coalescing agent (NMP or ethylene glycol) was added to facilitate preparation of membranes. Membranes were prepared and boiling water uptakes (%) determined as described above. Results are provided in Table H below.

Table H

Sulphonated Polymer from	Boiling Water Uptake (%)	Final Sulphonated Polymer conc. (% w/w)
1b	98	20.9
2a	123	20

15

Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or

25

process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

- 5 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each  
10 feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any  
15 novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. A method of preparing a formulation comprising an ion-conducting polymeric material, the method comprising:
- 5
- (a) selecting an ion-conducting polymeric material of a type which includes:
- (i) phenyl moieties;
- (ii) carbonyl and/or sulphone moieties; and
- 10 (iii) ether and/or thioether moieties;
- (b) selecting a solvent mixture comprising water and a first organic solvent in which mixture said ion-conducting polymeric material can be dissolved and/or
- 15 dispersed;
- (c) dissolving and/or dispersing said ion-conducting polymeric material in said solvent mixture;
- 20 (d) removing greater than 80% of the total amount of said first organic solvent in said solvent mixture, thereby to leave a formulation comprising said ion-conducting polymeric material dissolved and/or
- 25 dispersed in a solvent formulation comprising a major amount of water.
2. A method according to claim 1, wherein said first organic solvent selected in step (b) is water miscible at 25°C and has a boiling point of less than that of water.
- 30
3. A method according to claim 1 or claim 2, wherein said first organic solvent has up to 5 carbon atoms.

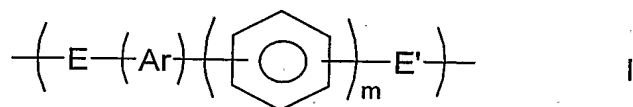


4. A method according to any preceding claim, wherein said first organic solvent includes an hydroxyl, ether or carbonyl functional group.
- 5 5. A method according to any preceding claim, wherein said first organic solvent is selected from acetone, methylethylketone, ethanol and tetrahydrofuran.
6. A method according to any preceding claim, wherein  
10 said solvent mixture includes an optional second organic solvent having a boiling point which is greater than that of said first organic solvent.
7. A method according to claim 6, wherein said second  
15 organic solvent has a boiling point at atmospheric pressure which is at least 20°C greater than the boiling point of said first organic solvent.
8. A method according to any preceding claim, wherein the  
20 ratio of the wt% of water to the wt% of said first organic solvent is in the range 0.25 to 2.5.
9. A method according to any preceding claim, wherein said solvent mixture of step (c) includes at least 1wt%  
25 and less than 20wt% of said ion-conducting polymeric material.
10. A method according to any preceding claim, wherein step (c) of the method is carried out at a temperature  
30 which is less than the boiling point of the solvent mixture.

11. A method according to any preceding claim, wherein after removal of the first organic solvent the solvent formulation which includes a major amount of water includes at least 10wt% and less than 30wt% of said ion-conducting polymeric material.

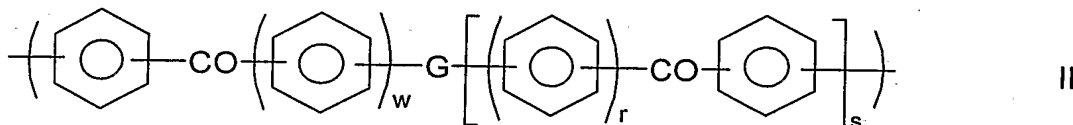
12. A method according to any preceding claim, wherein said ion-conducting polymeric material includes:

a moiety of formula

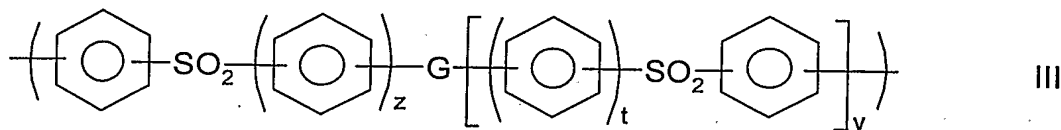


and/or a moiety of formula

15

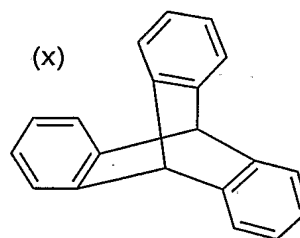
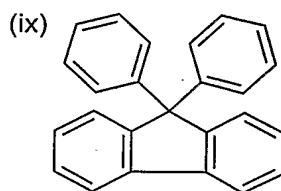
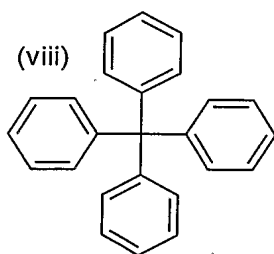
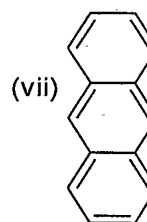
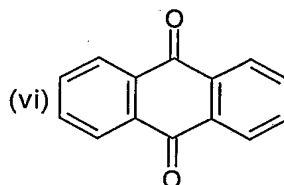
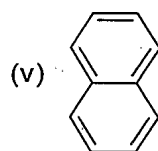
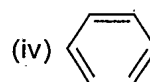
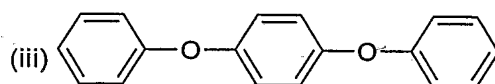
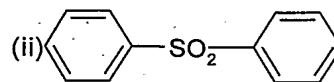
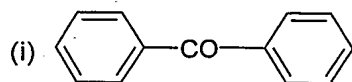
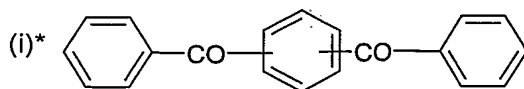


and/or a moiety of formula



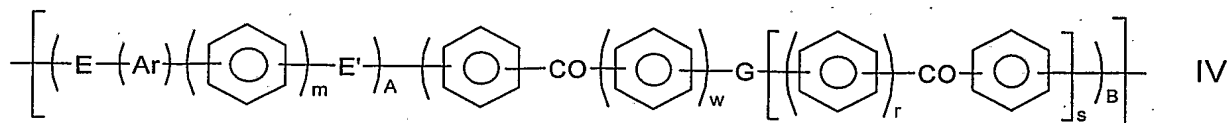
20

wherein at least some of the units I, II and/or III are functionalised to provide ion-exchange sites, wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and  
5 wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from  
10 one of the following moieties (i)\* or (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

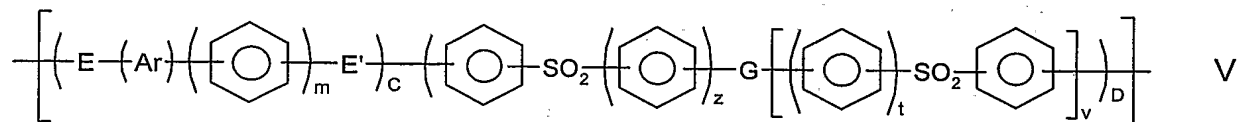


13. A method according to any preceding claim, wherein said polymeric material is sulphonated.

5 14. A method according to any preceding claim, wherein said polymeric material is a homopolymer having a repeat unit of general formula

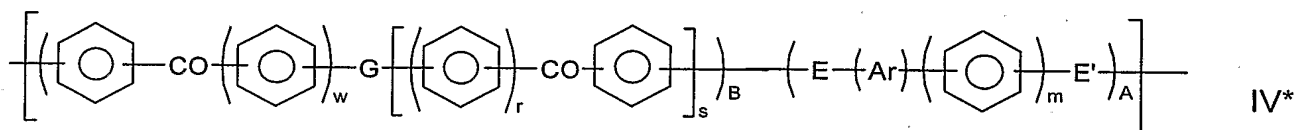


or a homopolymer having a repeat unit of general formula



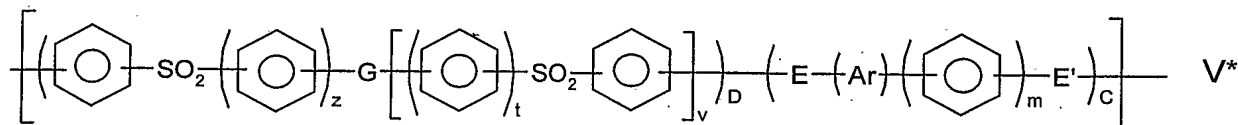
or a random or block copolymer of at least two different units of IV and/or V provided that repeat units (or parts of repeat unit) are functionalised to provide ion-exchange sites;

or a homopolymer having a repeat unit of general formula



10

or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV\* and/or V\* provided that repeat units (or parts of repeat units) are functionalised to provide ion-exchange sites;

15

wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in claim 12.

5 15. A method according to any preceding claim, wherein said ion-conducting polymeric material includes at least some ketone moieties in the polymeric chain.

10 16. A method according to any preceding claim, wherein said ion-conducting polymeric material includes -ether-biphenyl-ether-phenyl-ketone-units.

15 17. A polymeric material containing formulation (hereinafter "said pmc formulation") which comprises an ion-conducting polymeric material dissolved and/or dispersed in a solvent formulation wherein:

(a) said ion-conducting polymeric material includes:

- 20 (i) phenyl moieties;  
(ii) carbonyl and/or sulphone moieties; and  
(iii) ether and/or thioether moieties; and

(b) greater than 50 wt% of said solvent formulation is made up of water.

25

18. A polymeric material according to claim 17, wherein said PMC formulation includes at least 9wt% of said ion-conducting polymeric material.

30 19. A method of fabricating an article, the method including the step of contacting a member with a formulation as described in any preceding claim.

20. A method according to claim 19, which is used to deposit the polymeric material on said member.

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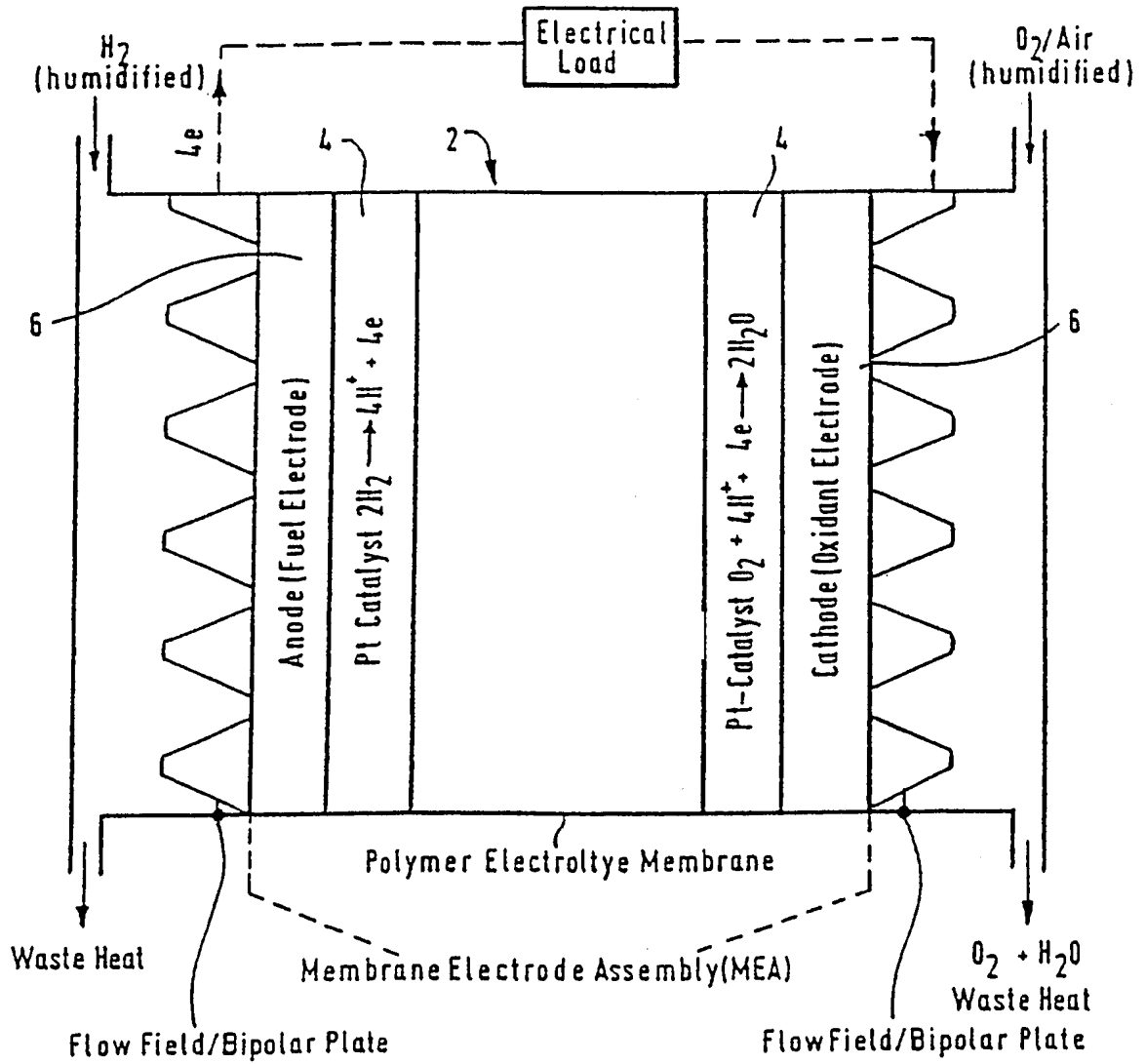


FIG.1.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB2004/001375

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01B1/12 B01D71/68

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 03/028140 A (LOCKLEY JOHN EDWARD ; VICTREX MFG LTD (GB); WILSON BRIAN (GB)) 3 April 2003 (2003-04-03) table B	1-20
A	EP 0 277 834 A (HYDRANAUTICS) 10 August 1988 (1988-08-10) table 1	1-20
A	EP 0 202 849 A (ICI PLC) 26 November 1986 (1986-11-26) page 9, line 10 - line 28	1-20
A	EP 0 145 305 A (ICI PLC) 19 June 1985 (1985-06-19) examples 1-20	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

20 July 2004

Date of mailing of the international search report

26/07/2004

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB2004/001375

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**PUB-NO:** WO2004088673A1  
**DOCUMENT-IDENTIFIER:** WO 2004088673 A1  
**TITLE:** ION-CONDUCTING  
POLYMERIC MATERIALS  
**PUBN-DATE:** October 14, 2004

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**APPL-NO:** GB2004001375

**APPL-DATE:** April 1, 2004

**PRIORITY-DATA:** GB00307606A (April 2, 2003)

**INT-CL (IPC):** H01B001/12 , B01D071/68

**ABSTRACT:**

CHG DATE=20041026 STATUS=O>A method of preparing a relatively stable solution and/or dispersion of an ion-conducting polymeric material, for example one comprising phenyl moieties, carbonyl and/or sulphone moieties and ether and/or thioether moieties, comprises: (a) selecting a solvent mixture comprising water and a first organic solvent in which mixture said ion-conducting polymeric material can be dissolved and/or dispersed; (b) dissolving and/or dispersing said ion-conducting polymeric material in said solvent mixture; and (c) removing greater than 80% of the total amount of said first organic solvent in said solvent mixture, thereby to leave a formulation comprising said ion-conducting polymeric material dissolved and/or dispersed in a solvent formulation comprising a major amount of water.